

Abstract No. Yang0275

Crystal Structure Changes of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ Cathode Materials During Charge and Discharge Studied by Synchrotron Based *In Situ* XRD

X.Q. Yang and J. McBreen (BNL), W-S. Yoon and C. Grey (SUNY, Stony Brook)

Beamline(s): X18A

Introduction: In the last 10 years, various lithiated transition metal oxides have been synthesized and investigated as alternative cathode materials for rechargeable lithium batteries to replace the widely used LiCoO_2 material. Recent studies on the new layer-structured $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ materials reported by Ohzuku¹ and Lu *et al.*² are very interesting since the combination of nickel and manganese may provide advantages such as low cost and toxicity, high thermal stability and capacities. Although a hexagonal structure similar to that of LiNiO_2 has been reported for the pristine materials, no detailed studies have been published on the structural changes of these new materials that occur during charge-discharge. Using synchrotron based *in situ* x-ray diffraction technique, we have studied the structural changes of this new $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ material during charge-discharge cycling in this work.

Methods and Materials: $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders were synthesized by reacting stoichiometric quantities of a co-precipitated double hydroxide of manganese and nickel with lithium hydroxide at 900 °C for 24 h in O_2 . Cathodes were prepared by slurring the active material powder with 10 wt% PVDF (KynarFlex 2801, Atochem), and 10 wt% acetylene black in a NMP(n-methyl pyrrolidone) solution, then coating the mixture onto an Al foil. After vacuum drying at 100 °C for 12 hours, the electrode disks (2.8 cm²) were punched and weighed (29 mg of active material for the data presented in this paper). The cathodes were incorporated into cells with a Li foil negative electrode, a Celgard separator and a 1 M LiPF_6 electrolyte in a 1:1 EC:DMC solvent (LP 30 from EM Industries Inc.). The cells were assembled in an argon-filled glove box. Mylar windows were used in these *in situ* cells, as has been described in detail elsewhere³. *In situ* XRD studies: *In situ* XRD spectra were collected on beam line X18A (using $\lambda=1.195$ Å wavelength) at the National Synchrotron Light Source. The step size of 2θ scan was 0.02 degrees in the regions with Bragg reflections and 0.05 degrees in the regions without reflections. The XRD spectra were collected in transmission mode.

Results: The structural changes of a $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ material during charge and discharge studied in this paper have several interesting features. The charge-discharge process above 2 V is accompanied by a reversible phase transition between H1 to H2, similar to the LiNiO_2 system. However, the formation of the H3 phase that occurs at voltages above 4.3 V in the LiNiO_2 system is suppressed. This may contribute to the higher thermal stability of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$.

Conclusions: The role of the effect of the higher degree of cation mixing in these systems (in c.f. to LiNiO_2) as suggested by our recent lithium NMR results and the effect of this structural disorder on the phase transitions and the consequent electrochemical properties still requires further investigation. The structural changes to an amorphous like state during the extended discharge around 1-V plateau may not be a reversible process and further studies are in progress to investigate this process in more detail.

Acknowledgments: We thank Steve Ehrlich for his help at Beam Line X18A of NSLS. The work done at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division, USDOE under Contract Number DE-AC02-98CH10886. The work done at SUNY Stony Brook was supported by the National Science Foundation (DMR 9901308).

References:

1. T. Ohzuku and Y. Makimura, Chemistry Letters (2001) 744.
2. Z. Lu, D. D. MacNeil, and J. R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A191.
3. M. Balasubramanian, X. Sun, X. Q. Yang, and J. McBreen, J. Power Sources 92 1 (2001) 1.